

Supplementary information for:

## On how ancillary ligand substitution affects charge carrier dynamic on dye-sensitized solar cell

Hashem Shahroosvand , Saeid Abaspour, Babak Pashaei , Babak Nemati Bideh

### ESI.S1 Experimental Section

**S1. Materials.** 5-tetrazole 1,10-phenanthroline (Tzphen) precursor complex were synthesized according to literature procedures.

Other materials in the syntheses were of reagent grade and used without further purification. (**Caution!** Sodium azide is potentially explosive and should be handled with much care.)

2,2'-bipyridine (bpy), 4,4'-di-methyl-2,2'-bipyridine (dmbpy), 1,10 phenanthroline (phen) ligands was purchased from Sigma-Aldrich and Merck. Nuclear magnetic resonance (<sup>1</sup>HNMR) spectra were recorded on a Bruker 250 MHz spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were obtained on Elementar Vario CHN analyzer. IR spectroscopy studies were performed on a FT-IR spectrophotometer in the 400- 4000 cm<sup>-1</sup> region (w, weak; b, broad; m, medium; s, strong). UV-vis absorption spectra in N, N dimethylformamide (DMF) solution were recorded on a 160 Shimadzu UV-vis spectrophotometer. Photoluminescence (PL) emissions spectra were recorded with an ocean optic USB2000 spectrophotometer. Cyclic voltammograms were measured using an SAMA500 electro analyzer with NOVA electrochemical software. Analyte solutions were prepared using N<sub>2</sub> saturated dry N, N dimethylformamide (DMF). All measurements were conducted at room temperature under a stream of dry N<sub>2</sub> at potential scan rates ranging from 50 to 500 mVs<sup>-1</sup>. 0.1 molL<sup>-1</sup>tetrabutylammoniumperchlorate (TBAP) in DMF solutions was used as a supporting electrolyte, with a typical solution concentration of 0.2 mol dm<sup>-3</sup>. The working electrode was a platinum disc, with platinum wire utilized as the counter

electrode. The reference electrode was Ag/AgCl, being chemically isolated from the analyte solution by an electrolyte containing bridgetube tipped with a porous frit. Ferrocene was employed as an internal reference, with all potentials quoted relative to the Fc<sup>+</sup>/Fc couple.

## S2. Synthesis and Characterization

5,6-epoxy-1,10-phenanthroline and 5-cyano-1,10-phenanthroline was prepared according to our previous publication.

**S2.1 5-(2H-Tetrazol-5-yl)-1,10-phenanthroline (Tzphen).** The Tzphen ligand was performed according to the procedure reported in previous work [1]. 5-Cyano-1,10-phenanthroline (410 mg, 2.0 mmol), NH<sub>4</sub>Cl (135 mg, 2.5 mmol), and NaN<sub>3</sub> (160 mg, 2.5 mmol) in *N,N*-dimethylformamide (10 mL) were stirred and heated at 140 °C for 48 h. The cooled mixture was poured into H<sub>2</sub>O (200 mL) and filtered. The filtrate was acidified to pH =3.5 with concentrated hydrochloric acid. After stirring for 5 h, the suspension was filtered. The resulting solid was washed with H<sub>2</sub>O (2 × 5 mL) and dried in vacuum over P<sub>2</sub>O<sub>5</sub> at room temperature. Yield: 54%. FT-IR (cm<sup>-1</sup>): 3392 (m), 3069 (m), 1602 (s), 1545 (s), 1418 (w), 867 (m), 727 (w). <sup>1</sup>H NMR (250 MHz, DMSO): δ 9.3 (d, J=8.5 Hz, 1H), 9.2 (d, J=8.5 Hz, 1H), 8.8 (s, 1H), 8.6 (d, J=6.5 Hz, 1H), 8.65 (d, J=6.5 Hz, 1H), 7.9 (t, J= 5.5 Hz, 1H), 7.8 (t, J=5.5 Hz, 1H). Anal. Calcd for C<sub>13</sub>H<sub>8</sub>N<sub>6</sub>: C, 56.722; H, 4.032; N, 30.533. Found: C, 56.731; H, 4.041; N, 30.545.

## S2.2 Synthesis of 2,2'-bipyridine-4,4'-dicarboxylic acid, dcbH2

The compound 2,2'-bipyridine-4,4'-dicarboxylic acid (dcbH2) were synthesized according to the literature procedure.[2]. Briefly, 3.23 g (17.55 mmol) of 4,4'-dimethyl-2,2'-bipyridine was added to the solution of 11.80 g (39.6 mmol) of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> that was dissolved in 45 mL of concentrated H<sub>2</sub>SO<sub>4</sub>, and the mixture was stirred for 30 min in an ice bath. The resulting solution was added to 410 mL of cold water, the solid was removed, and 50 mL of water was added. The solid was dissolved by adding 10% NaOH until pH 10. The final product was precipitated by adding 2.0 mol L<sup>-1</sup> HCl to the solution until it reached pH 2, and the white solid was collected. Yield: 93% *Anal.* Calc. for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>: C, 59.02; H, 3.304; N, 11.47%. Found: C, 59.031; H, 3.309; N, 11.478%

**S2.3 [Ru(dcbpy)<sub>2</sub>(Tzphen)]<sup>+2</sup> (S1)** Ru L<sub>2</sub>C<sub>12</sub>H<sub>2</sub>O was obtained by refluxing under nitrogen atmosphere 26 mg (1 mmol) of RuCl<sub>3</sub>·3H<sub>2</sub>O, and 44.8 mg (2 mol) of ligand dcbpy in 20 mL of DMF for 8 h. After cooling, traces of RuL<sub>3</sub> were filtered. Most of the DMF solvent was evaporated under vacuum, and RuL<sub>2</sub>Cl<sub>2</sub> was precipitated with acetone. The crystals were filtered off and dried in vacuum [3].

[Ru(dcbpy)<sub>2</sub>(Tzphen)]<sup>+2</sup> was synthesized as follows: 283 mg (0.428 mmol) of Ru(dcbpy)<sub>2</sub>Cl<sub>2</sub>H<sub>2</sub>O was dissolved in 30 mL of DMF under reduced light. Tzphen (32 mg, 1.2 mmol) was separately dissolved in 2 mL of DMF and subsequently added to the above solution. The reaction mixture was then heated to reflux for 6 h under nitrogen atmosphere, while magnetic stirring was maintained. After this time, the reaction mixture was allowed to cool, and the solvent was removed on a rotary evaporator. The resulting solid was dissolved in H<sub>2</sub>O and filtered through a sintered glass crucible. The filtrate was placed in a refrigerator overnight. After reaching room temperature, the microcrystalline solid was isolated by suction filtration, washed well with H<sub>2</sub>O/acetone-ether solution (1: 10) followed by anhydrous diethyl ether, and air-dried for an hour (yield 80%) [4]. Anal. Calcd for C<sub>37</sub>H<sub>24</sub>Cl<sub>2</sub>O<sub>8</sub>RuN<sub>10</sub> (1036.62): C, 42.867; H, 2.316; N, 13.515%. Found: C, 42.892; H, 2.345; N, 13.530%. <sup>1</sup>H NMR (DMSO, 250 MHz, δ/ppm): 10.08 (d, J = 5.8 Hz; 1H); 9.90 (d, J = 6.0 Hz; 1H); 9.36 (s, 1H); 9.19 (s, 1H); 8.79 (d, J = 5.8 Hz; 1H); 8.60 (d, J = 5.8 Hz; 1H); 8.54 (d, J = 6.0 Hz; 1H); 8.41 (s, 1H); 8.40 (s, 1H); 8.28-8.32 (m, 4H); 8.01 (d, J = 5.8 Hz; 1H); 7.83 (d, J = 9.5 Hz; 1H); 7.71 (d, J = 9.5 Hz; 1H); 7.63-7.67 (m, 2H); 7.49- 7.55 (m, 2H); 7.42-7.46 (m, 3H); 7.26-7.38 (m, 5H).

#### **S2.4 [Ru(L)(bpy)(dcbpy)]<sup>+2</sup> (S2)**

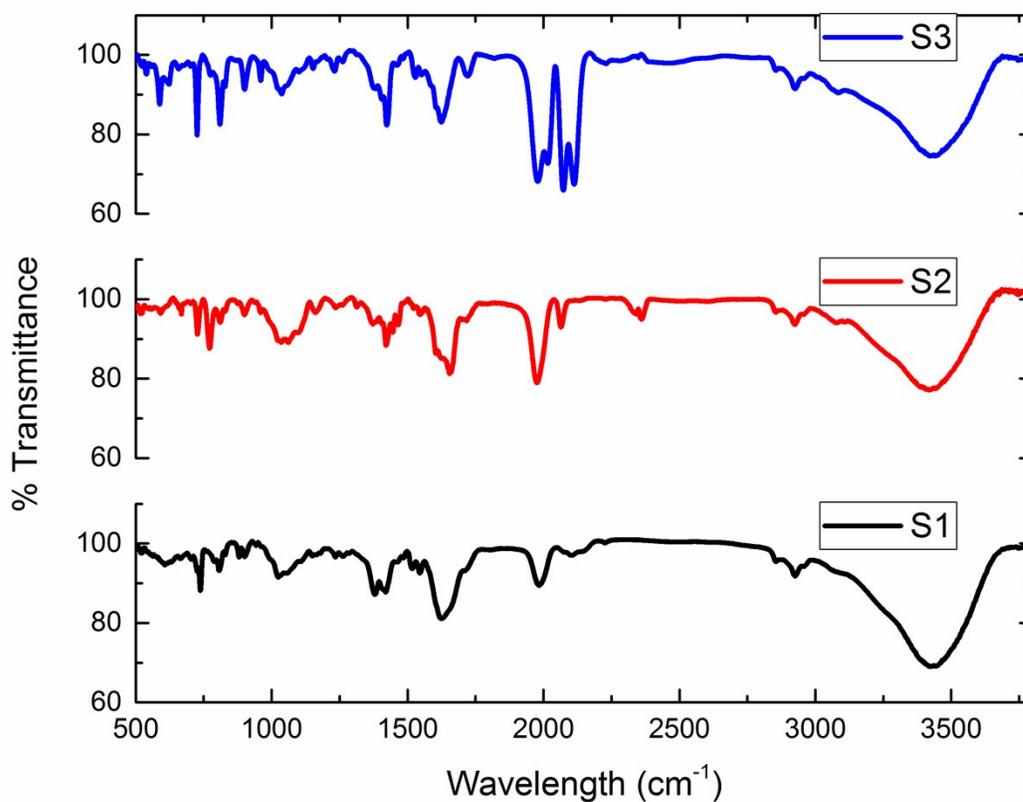
A solution of 0.026 g of RuCl<sub>3</sub>·3H<sub>2</sub>O (1 mmol) and 0.032g of Tzphen (1.2 mmol) in 30 mL DMF was refluxed with continuous stirring for 5 h under nitrogen atmosphere. The reaction mixture with 0.032g bpy (1.2 mmol) was again refluxed with continuous stirring at 150 °C for 4 h under nitrogen atmosphere. Finally, 0.028 g of dcbpy (1.2 mmol) was added, the temperature was decreased to 140 °C, and the reaction was kept under these conditions for 4 h, which allowed it to proceed to completion. The compound was purified by concentrating the obtained solution,

washed and filtered with ultrapure H<sub>2</sub>O. The obtained solid was dried in a vacuum oven and weighed 0.21 mg. Yield = 39%. *Anal.* Calc. for C<sub>35</sub>H<sub>24</sub>N<sub>10</sub>Cl<sub>2</sub>O<sub>8</sub>Ru (948.60): C, 44.313; H, 2.531; N, 14.769%. Found: C, 44.339; H, 2.570; N, 14.782%. <sup>1</sup>H NMR (DMSO, 250 MHz, δ/ppm): 10.08 (d, J = 5.8 Hz; 1H); 9.90 (d, J = 6.0 Hz; 1H); 9.36 (s, 1H); 9.19 (s, 1H); 8.79 (d, J = 5.8 Hz; 1H); 8.60 (d, J = 5.8 Hz; 1H); 8.54 (d, J = 6.0 Hz; 1H); 8.41 (s, 1H); 8.40 (s, 1H); 8.28-8.32 (m, 4H); 8.01 (d, J = 5.8 Hz; 1H); 7.83 (d, J = 9.5 Hz; 1H); 7.71 (d, J = 9.5 Hz; 1H); 7.63-7.67 (m, 2H); 7.49-7.55 (m, 2H); 7.42-7.46 (m, 3H); 7.26-7.38 (m, 5H).

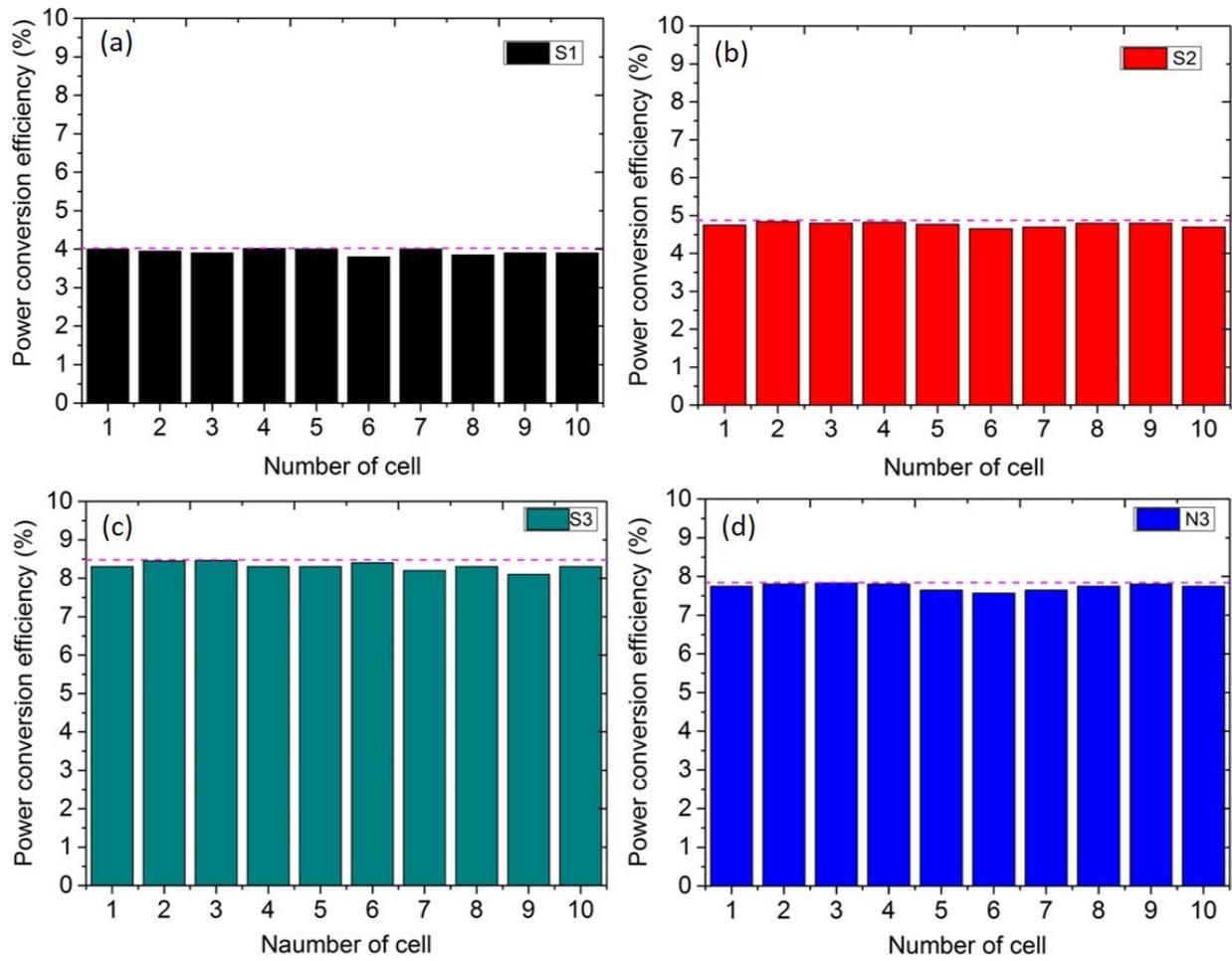
**S2.5 Synthesis of [Ru(Tzphen)(dcbH<sub>2</sub>)(NCS)<sub>2</sub>](S3)** The RuCl<sub>3</sub> (0.026 g, 1 mmol), was dissolved in 50 mL of N,N'-dimethylformamide and 0.032 g of Tzphen (1.2 mmol) was added. The mixture was kept at 140 °C for 4 h under nitrogen atmosphere. After this period, 0.028 g of dcbH<sub>2</sub> (1.2 mmol) was added to the mixture, and the temperature was increased to 160 °C and was kept at this level for 4 h. Finally, 0.044 g of NaNCS (5 mmol) was added, the temperature was decreased to 140 °C, and the reaction was kept under these conditions for 4 h, which allowed it to proceed to completion. The compound was purified by concentrating the obtained solution, washed and filtered with ultrapure H<sub>2</sub>O. The main fraction was concentrated, precipitated by adding H<sub>2</sub>SO<sub>4</sub> (0.5 mol L<sup>-1</sup>) to reach pH ~ 1.0 and, finally, filtered. The obtained solid was dried in a vacuum oven and weighed 0.21 mg. Yield = 39%. *Anal.* Calc. for C<sub>27</sub>H<sub>16</sub>N<sub>10</sub>O<sub>4</sub>S<sub>2</sub>Ru (709.68): C, 45.692; H, 2.256; N, 19.741%. Found: C, 45.705; H, 2.289; N, 19.765%. <sup>1</sup>H NMR (DMSO, 250 MHz, δ/ppm): 10.08 (d, J = 5.8 Hz; 1H); 9.90 (d, J = 6.0 Hz; 1H); 9.36 (s, 1H); 9.19 (s, 1H); 8.79 (d, J = 5.8 Hz; 1H); 8.60 (d, J = 5.8 Hz; 1H); 8.54 (d, J = 6.0 Hz; 1H); 8.41 (s, 1H); 8.40 (s, 1H); 8.28-8.32 (m, 4H); 8.01 (d, J = 5.8 Hz; 1H); 7.83 (d, J = 9.5 Hz; 1H); 7.71 (d, J = 9.5 Hz; 1H); 7.63-7.67 (m, 2H); 7.49- 7.55 (m, 2H); 7.42-7.46 (m, 3H); 7.26-7.38 (m, 5H).

**S3.** The preparation of TiO<sub>2</sub> screen-printing pastes including 20 nm particle sized TiO<sub>2</sub> colloid and 400 nm microcrystalline-TiO<sub>2</sub> as the transparent and light scattering layers of the photoanode, fabrication of porous -TiO<sub>2</sub> electrode and preparation of counter Pt-electrodes were carried out according to literature [5]. The electrolyte employed was a solution of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.03 M I<sub>2</sub>, 0.10 M guanidinium thiocyanate and 0.5 M 4-tertbutylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15).

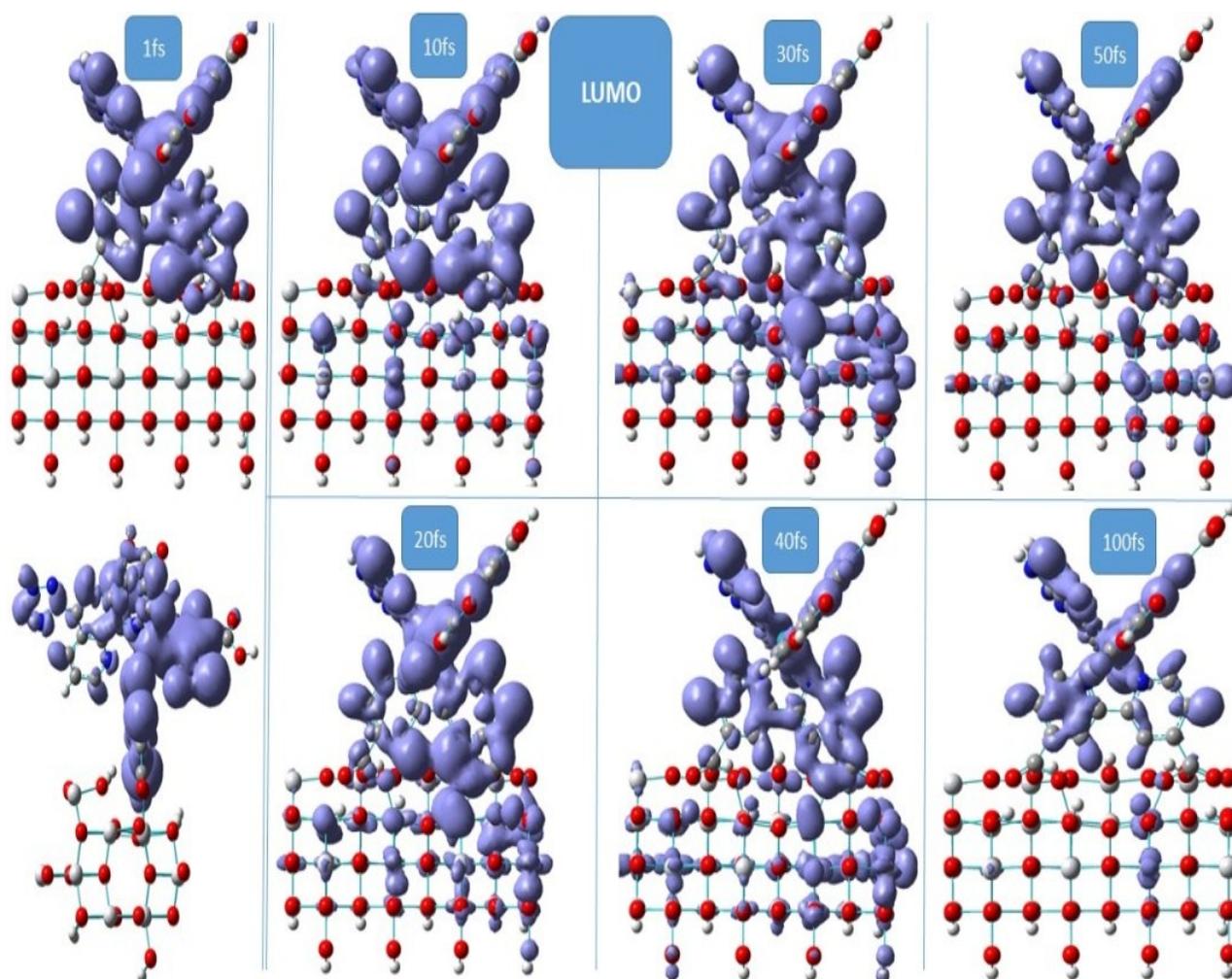
**S4 Photocurrent–voltage measurements** The photocurrent–voltage (I–V) characteristics were recorded using a computer-controlled Keithley 2400 source meter under air mass (AM) 1.5 simulated illumination ( $100 \text{ mW cm}^{-2}$ , Oriel, 67 005). The action spectra of the monochromatic incident photo-to-current conversion efficiency (IPCE) for the solar cells were performed using a commercial setup for IPCE measurement (PV-25 DYE, JASCO).



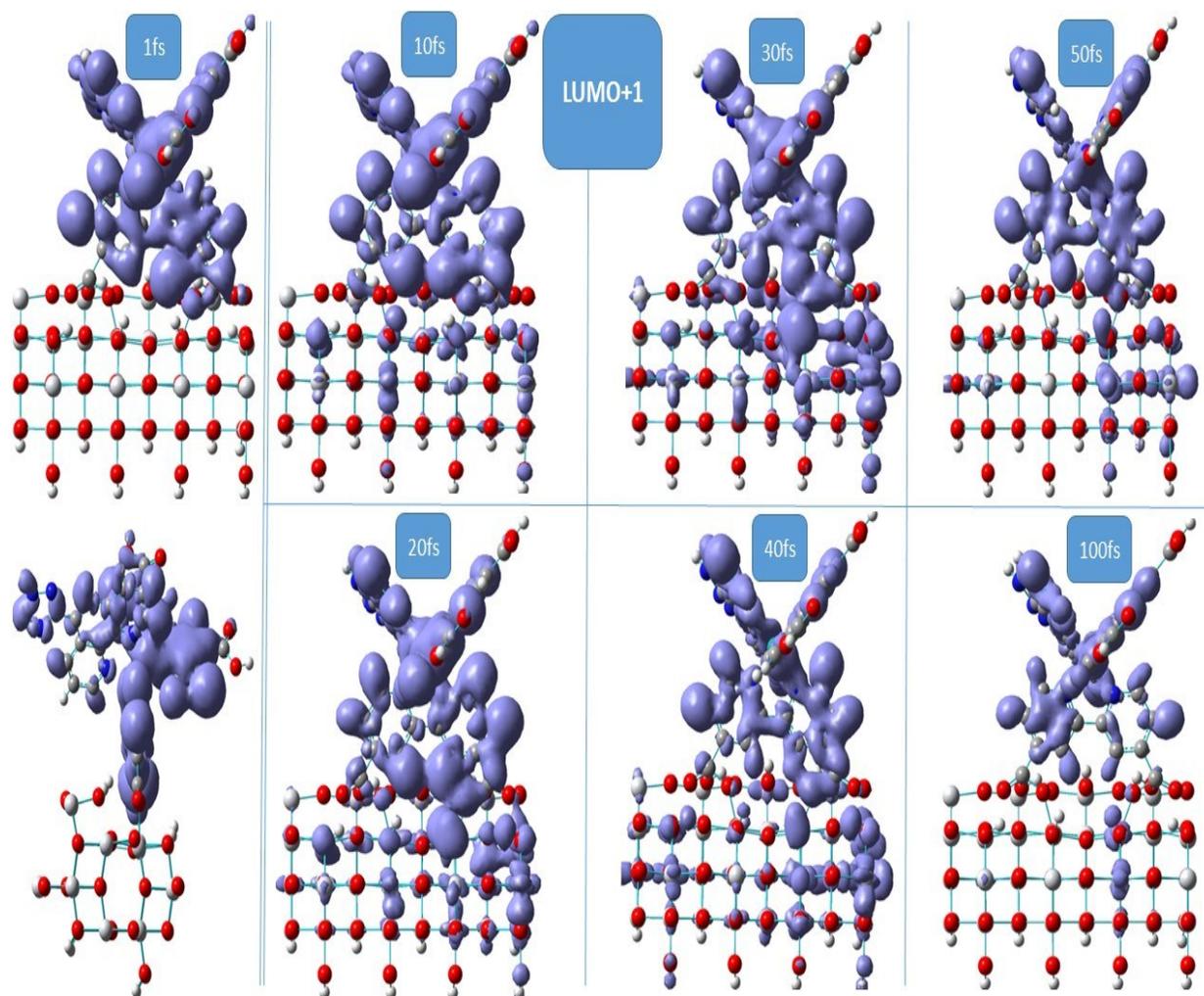
**Fig. S1** FT-IR spectra of (S1-S3) in KBr disc.



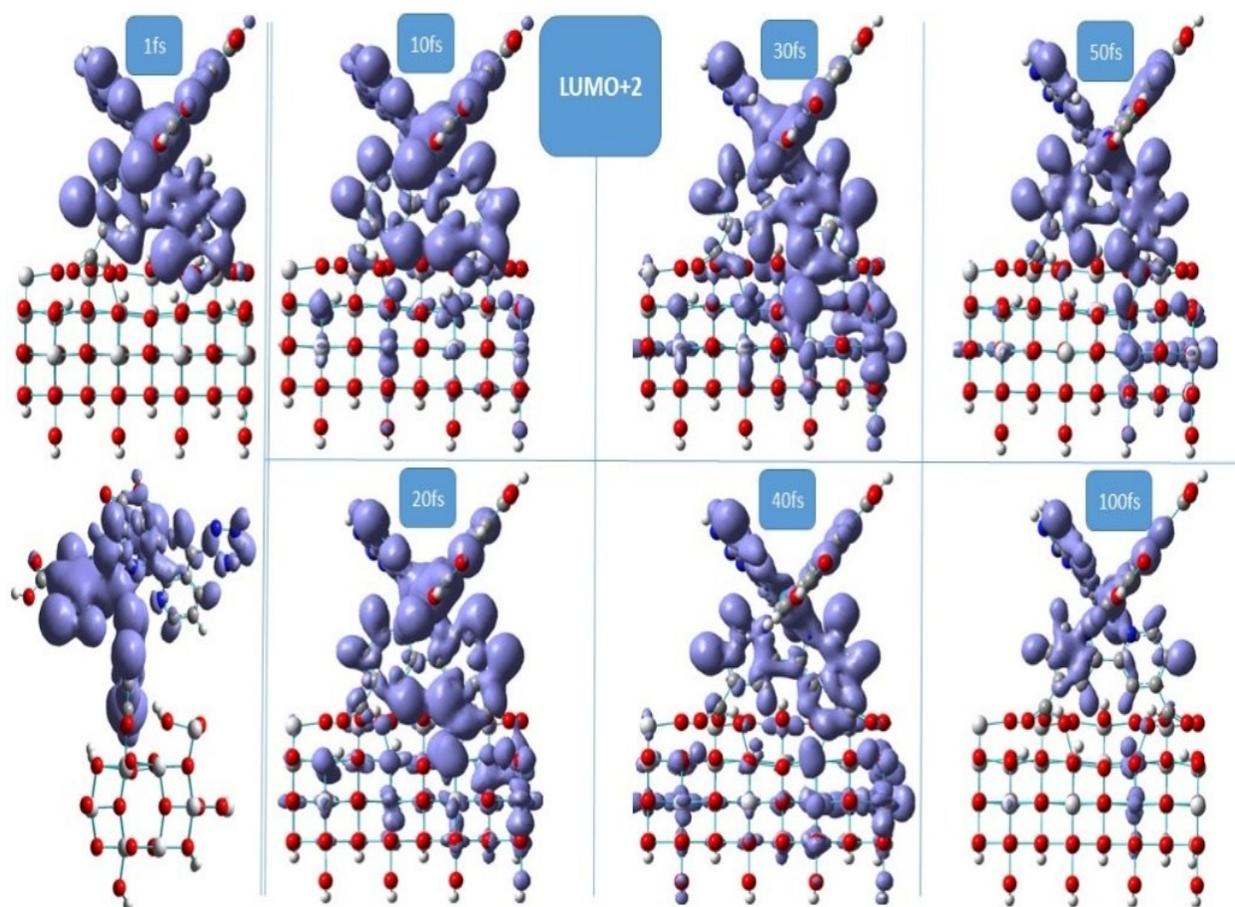
**Fig. S2.** Histogram depicting reproducibility of DSSC conversion efficiencies. Reported values of 10 DSSC devices.



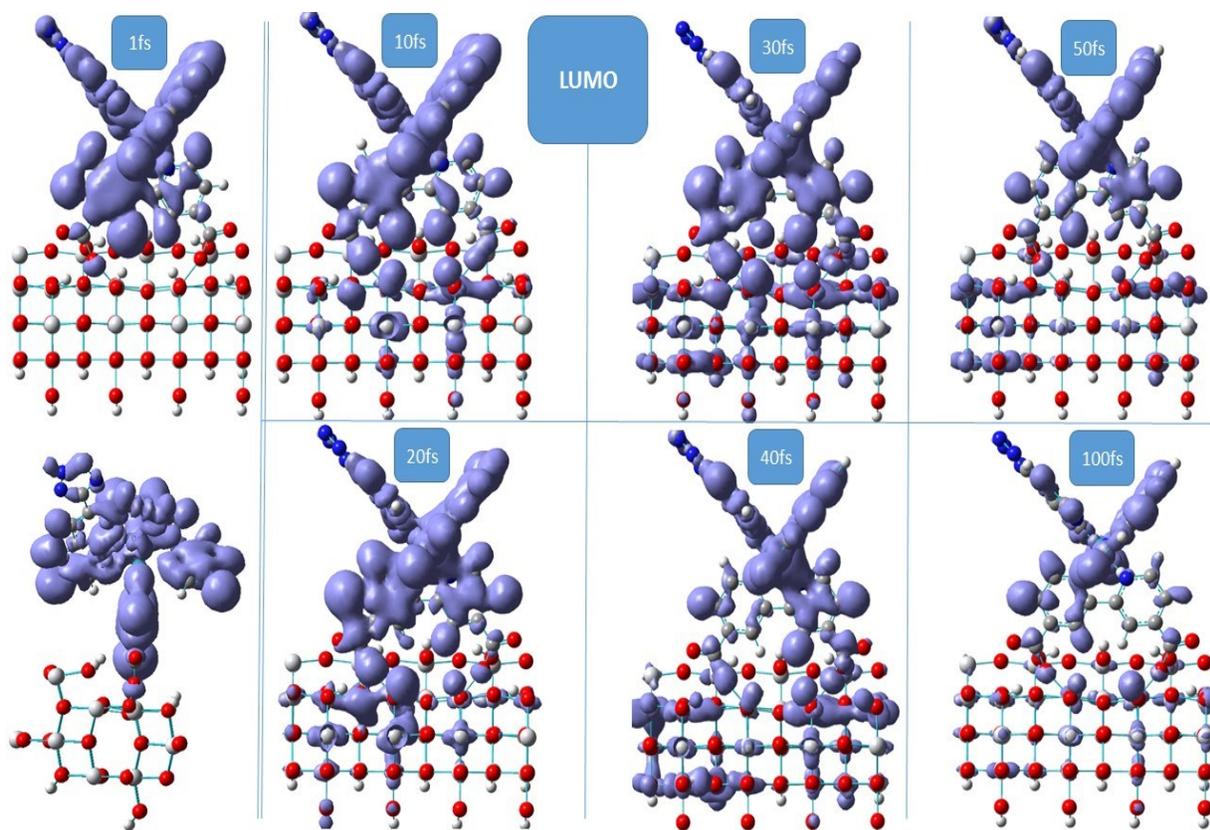
**Fig. S3** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO of (S1) attached to a pristine (101) surface. Only the local TiO<sub>2</sub> structure, next to the photoexcited adsorbate, is illustrated for the detailed view of the time-dependent charge distribution.



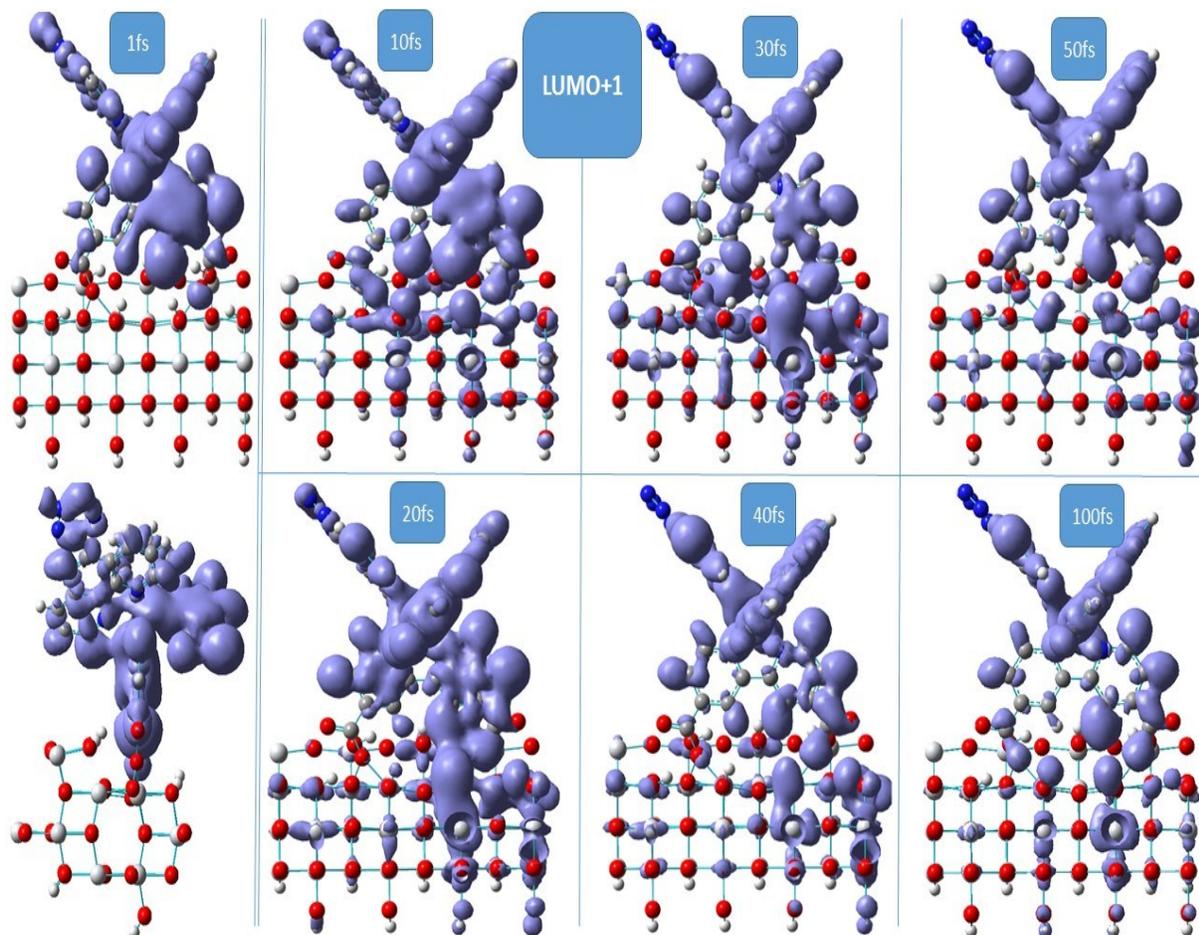
**Fig. S4** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO+1 of (S1) attached to a pristine (101) surface.



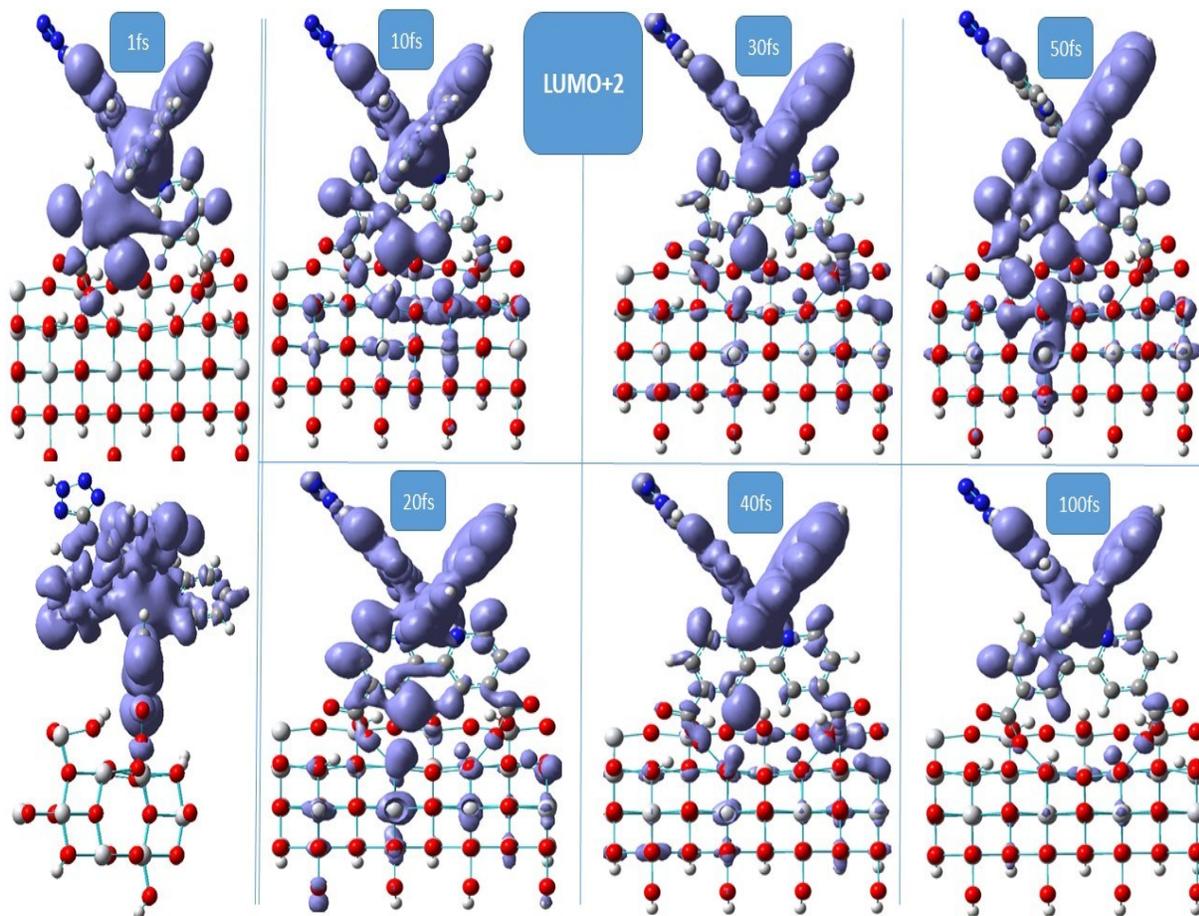
**Fig. S5** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO+2 of (S1) attached to a pristine (101) surface.



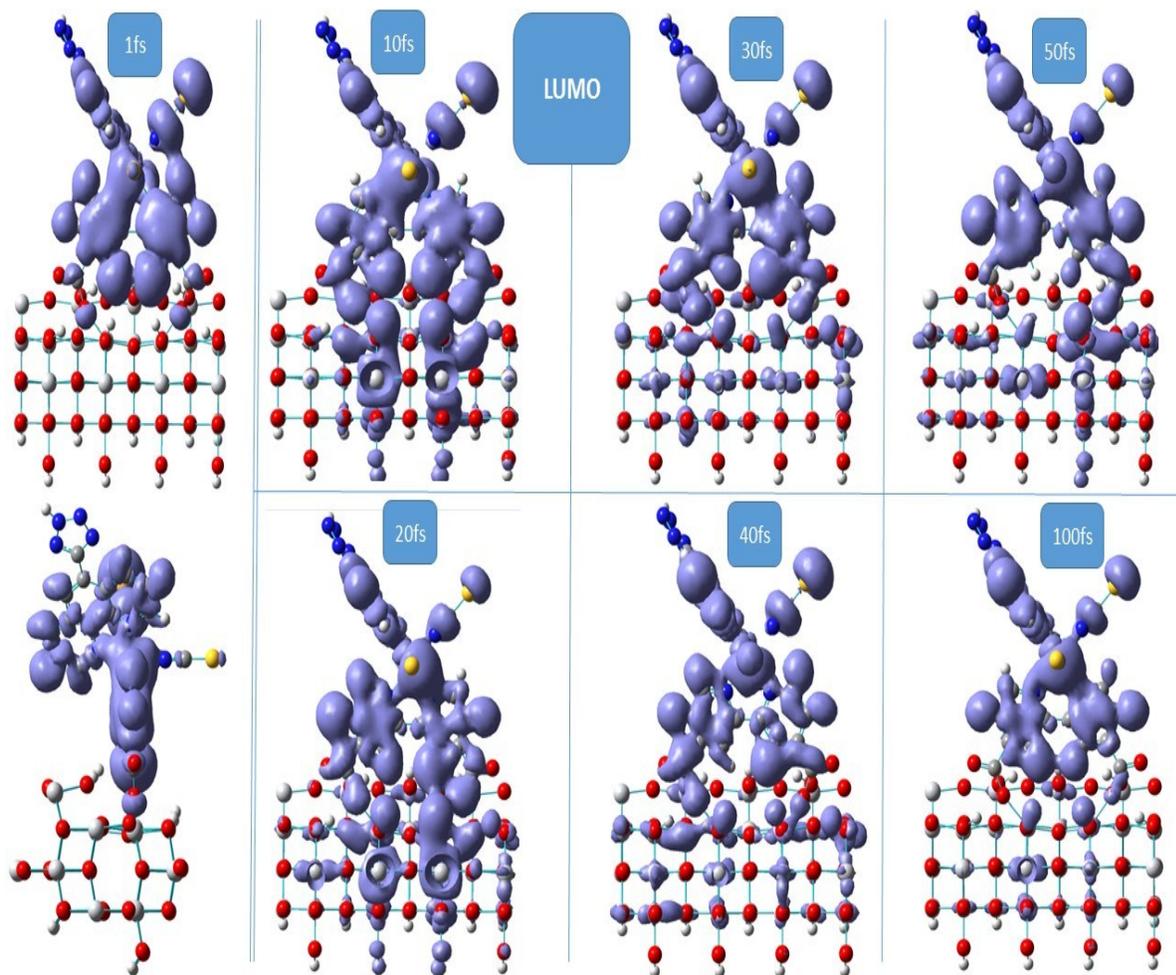
**Fig. S6** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO of (S2) attached to a pristine (101) surface.



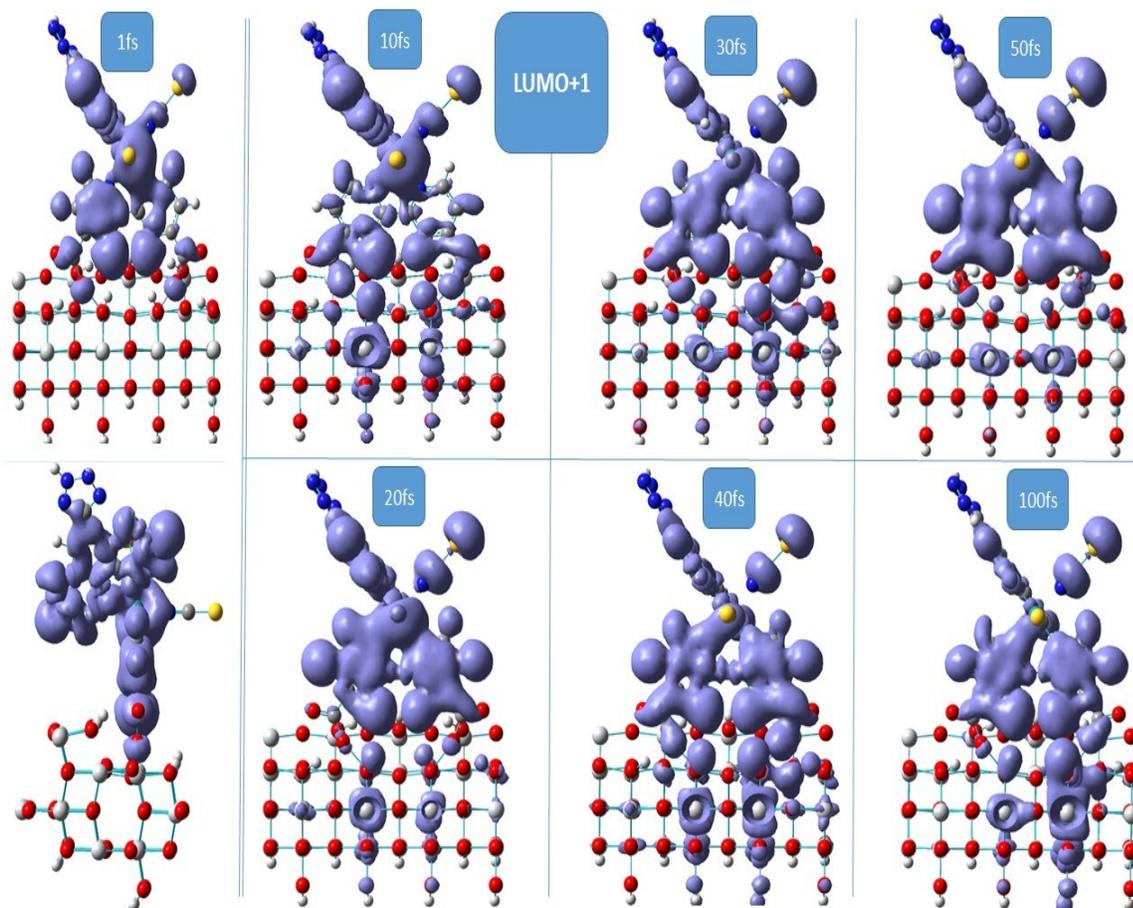
**Fig. S7** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO+1 of (S2) attached to a pristine (101) surface.



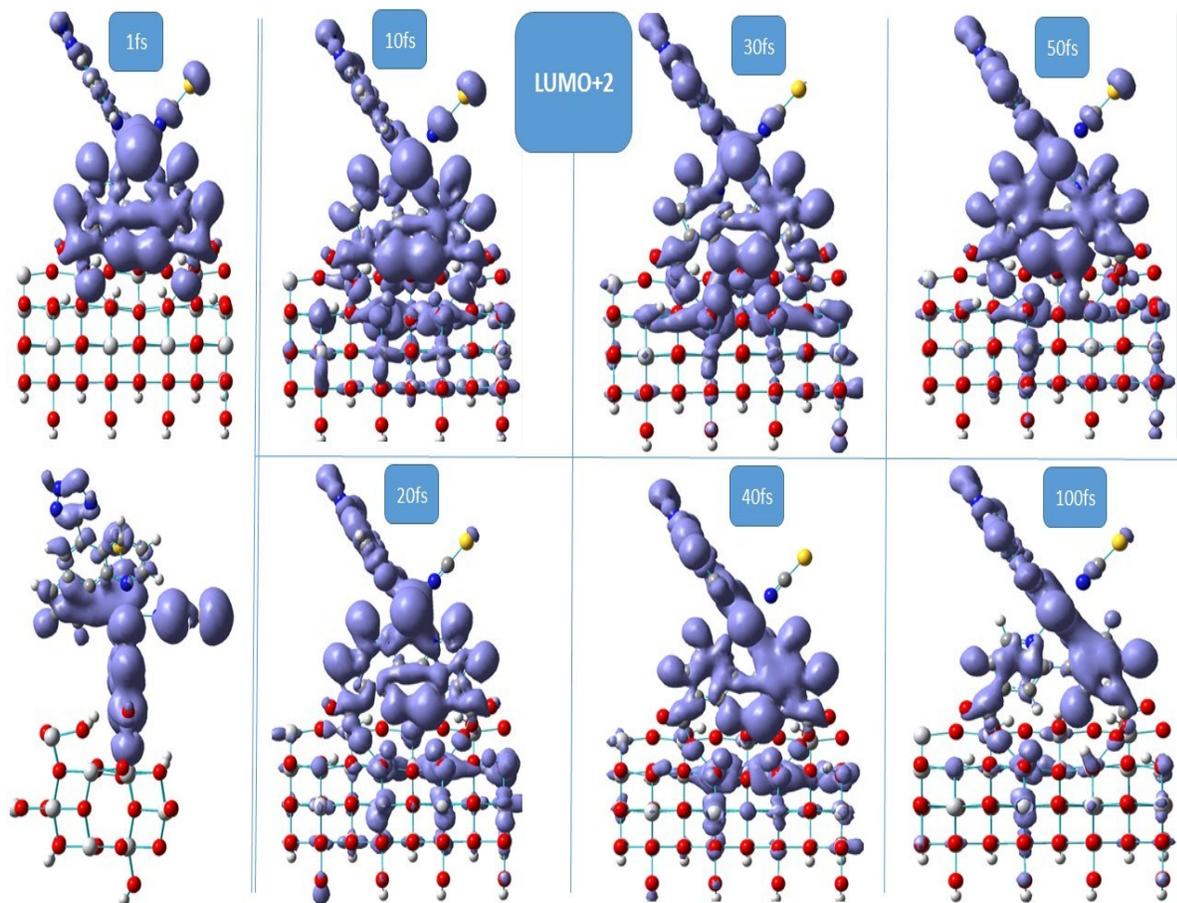
**Fig. S8** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO+2 of (S2) attached to a pristine (101) surface.



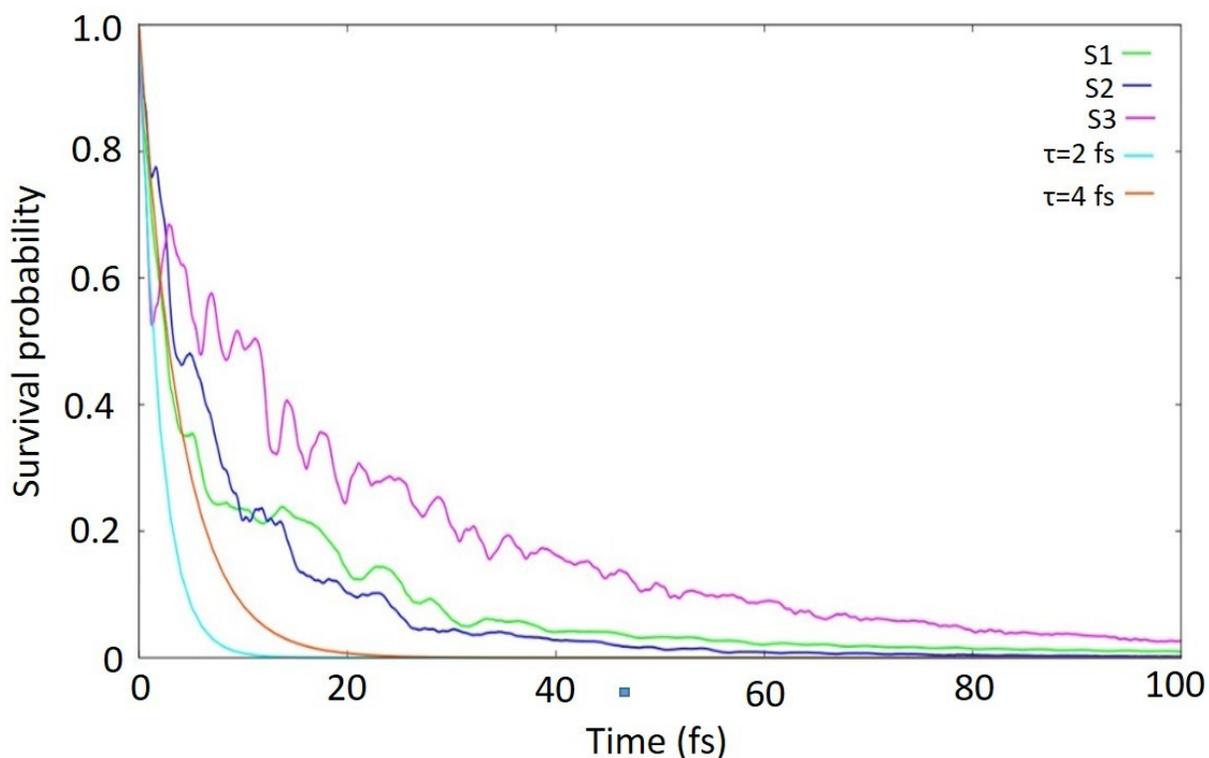
**Fig. S9** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO of (S3) attached to a pristine (101) surface.



**Fig. S10** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO+1 of (S3) attached to a pristine (101) surface.



**Fig. S11** Snapshots of the electronic charge distribution at 1 fs after initiating the IET from LUMO+2 of (S3) attached to a pristine (101) surface.



**Fig. S12** Computed survival probabilities corresponding to the photoexcited surface (S1-S3). Each curve represents the probability of the electron to remain in the respective photoexcited surface complex. The estimated lifetime of LUMO of (S1-S3) is obtained from the fitting of the survival probability with the bi-exponential decay model.

References:

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- [2] A.V. Müller, L. D. Ramos, K. P. M. Frin, K. T. de Oliveira, A. S. Polo, *RSC Adv.*, 2016, **6**, 46487.

[3] B. M. Trost, M. L. Miller, . *J. Am. Chem. SOC.* 1988, **110**, 3687.

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